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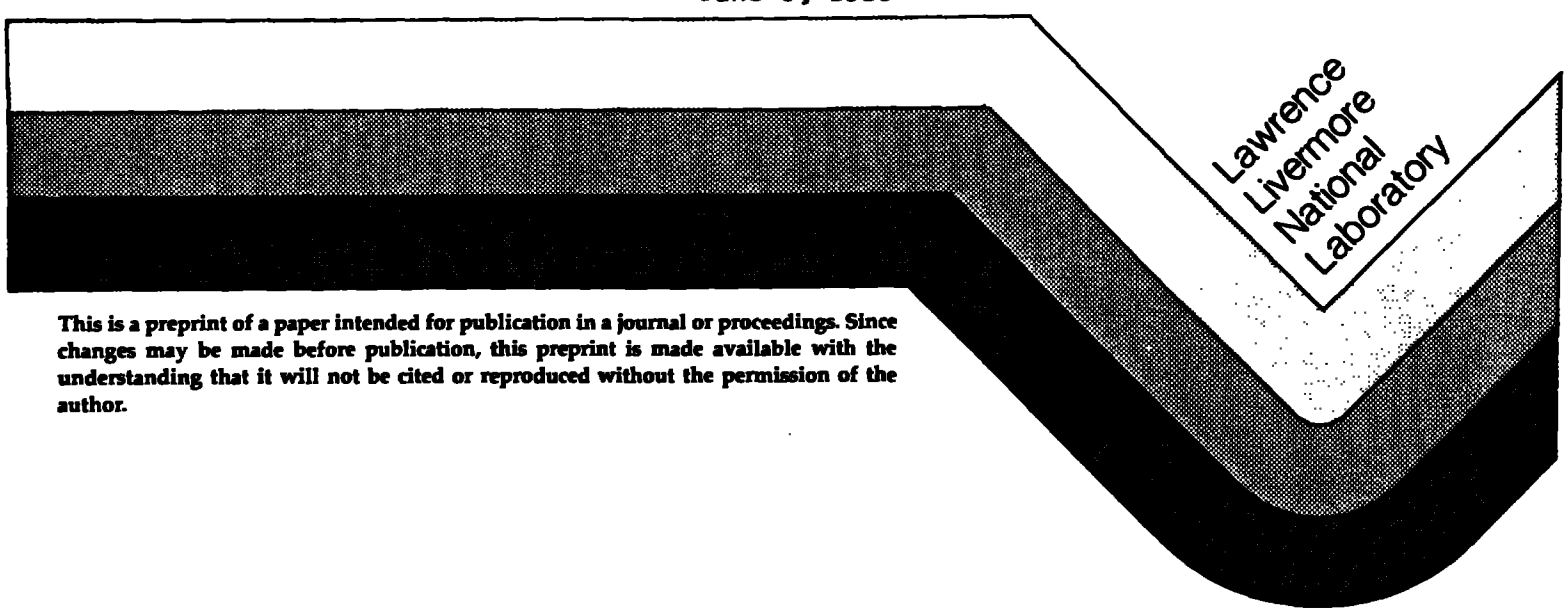

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THEORETICAL DESCRIPTION OF THE LOW-LYING EXCITED STATES OF CuCl*

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ABSTRACT

The low-lying excited states of CuCl have been investigated theoretically in the Hartree-Fock approximation. Spin-orbit interactions have been included semiempirically using an atoms-in-molecules technique. All six excited states that were previously characterized experimentally are found to arise from fine structure sublevels of the $Cu^+(3d^9 4s\ ^{1,3}D)Cl^-(3p^6\ ^1S)$ configuration.

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INTRODUCTION

The early theoretical work on CuCl dates back to the studies of Mulliken.[1] The pioneering experimental work was reported by Ritschl.[2] The majority of detailed spectroscopic analysis has been performed by Rao and coworkers,[3] supplemented by the work of Lagerqvist and Lazarava-Girsmoff[4] and Ahmed and Barrow.[5] Six emission band systems were characterized with the energies 2.36, 2.54, 2.56, 2.85, 2.86 and 3.14 eV. These were assigned as transitions terminating on the $X^1\Sigma^+$ state and originating from the $A^1\Pi$, $B^1\Pi$, $C^1\Sigma^+$, $D^1\Pi$, $E^1\Sigma^+$, and $F^1\Pi$ states, respectively. The Λ-doubling in these band systems attracted the particular interest of these investigators. The B/C and D/E interactions were described as arising from p_π/p_σ Van Vleck "pure precession." As dicussed below, the previous assignments need revision because investigators did not consider the effects of spin-orbit interaction and could determine only the Ω quantum number. Furthermore, all these excited states arise from the single configuration $Cu^+(3d^9 4s)Cl^-(3p^6)$, and hence the Λ-doubling cannot be of the p_π/p_σ type.

In the next section the choice of a basis set, spin-orbit coupling, and the expected electron correlation errors for the Cu^+ ion are dicussed. The final section presents the results for CuCl along with our assignments of the experimental spectra of both CuCl and CuF.

CALCULATIONAL DETAILS

The calculations reported here were performed using the Hay and Dunning[6] gaussian basis for Cl and three different gaussian basis sets for Cu. Basis I was constructed from Wachters[7] (14s11p5d) basis contracted

(62111111/511211/32) with the exponents optimized for the ^2S state. Basis II was generated by adding an additional 3d function with an exponent 0.1491 as suggested by Hay.[8] For basis III the 3d exponents were replaced with a set optimized for the ^2D state of Cu and contracted (411).[8] Table I compares the Hartree-Fock (HF) energies for these three basis sets to experiment.[9] The cancelation of basis set and electron correlation errors for basis sets I and II leads to apparent agreement with experiment for the $3d^{10}4s$, $^2S \rightarrow 3d^9 4s^2$, ^2D excitation energy. The 3d exponents and contraction of basis III have the flexibility to correctly describe the changes in the 3d shell upon excitation and leads to an energy difference in good agreement with numerical HF calculations.[10] This is the most accurate of the basis sets, however the disagreement with experiment for this transition is still 1.3 eV. Since the ionization energy does not involve a change in the 3d occupancy, all three basis sets give comparable results. For the $^{1,3}D$ Cu^+ excited states, which are relevant to CuCl, the HF error is 1.5 eV. It is important to note that because of the cancelation of basis set, electron correlation, and relativistic errors, the splitting of the ^3D and ^1D states agrees almost exactly with experiment. This accuracy of the HF excited state energy level pattern allows us to assign the CuCl spectra without including the large correlation errors.

The ^3D state of Cu^+ is split by spin-orbit coupling into the fine-structure components $^3D_{1,2,3}$. The reduction from spherical to cylindrcal symmetry in CuCl further splits the levels, with m_j or Ω being the only conserved angular momentum quantum number. In CuCl the spin-orbit interaction is expected to be energetically significant and must be included in our analysis. The rigorous inclusion of spin-orbit effects

remains a subject of active investigation.[11] Here we will use a simple atoms-in-molecules method that has been adopted in a number of studies of diatomic[12] and triatomic[13] systems.

For the fine-structure sublevels arising from the $Cu^+(^{1,3}D)Cl^-(^1S)$ states, we construct a spin-orbit hamiltonian, as shown in Table II. The electrostatic energies of the $^{1,3}\Lambda$ states are calculated first, and then the spin-orbit interaction over the $^{1,3}\Lambda_\Omega$ basis is expressed in terms of the atomic spin-orbit coupling parameter ($\zeta = -828cm^{-1}$ for Cu^+ ^3D).[9,14] Diagonalization of the resulting matrix yields approximations to the true energy levels.

RESULTS AND DISCUSSION

The HF energies in each of the basis sets for the low-lying states of CuCl are given in Table III. The internuclear separation was fixed at the calculated equilibrium value of 4.2 a.u. for each state. In addition to the excitation energies relative to the ground $X^1\Sigma^+$ state, the energy difference relative to the lowest triplet state are listed for each state. Analysis of the HF wavefunctions for each of the excited states shows that they are derived from a common configuration $Cu^+(3d^94s)Cl^-(3p^6)$. This is supported experimentally by the fact that all six excited states share a nearly common set of vibrational and rotational spectroscopic constants.[15] Consequently the energy differences among the excited states are in good agreement for each basis set. The calculated excitation energies relative to the ground state reflect the basis set, electron correlation, and relativistic errors discussed above for the Cu^+ free ion. Although the total number of calculated and experimental levels accidently agree, there is a shortage of $^1\Sigma^+$ and $^1\Pi$ states compared to the experimental assignments. Also the

pattern of excited levels is inconspicuous.

As described above, we may approximate the spin-orbit interactions by diagonalizing an effective spin-orbit hamiltonian constructed using the Cu^+ spin-orbit parameters. The results of this calculation are shown in Figure 1. The HF energies have been adjusted upward uniformly by 1.77 eV to obtain agreement with the lowest experimentally observed $\Omega = 0^+$ level. The agreement shown in Figure 2 for the relative energies is now nearly quantitative, and the pattern of the experimentally observed Ω-values is easily rationalized. Our calculations reverse the order of the E and D levels which stems from the fact that the $2\,^1\Sigma^+$ state was found from a frozen core HF calculation and is slightly too low in energy. The calculated energies are still in good agreement with experiment, and since the levels have different values of Ω, the reversal does not effect the assignments. The $\Omega = 0^-$, 2, and 3 states have not been observed experimentally, because they are not dipole connected to the ground 0^+ state. In Table IV we give recommended values for the excitation energies for these metastable states; these were obtained by combining the experimental energies for the optically allowed states with the semiemperical spin-orbit splittings shown in Figure 1.

The appropriateness of this energy level scheme is further supported by the straightforward reassignment it makes possible for the excited states of the analogue copper halide CuF. Steele and Broida[16] have identified several band systems in CuF, and as shown in Table IV, these systems arise from nearly the same pattern of energy levels found in CuCl. We anticipate that the spectra of CuBr and CuI can be similarly explained. However, the experimental work to date[17] is not sufficiently complete to make unique assignments possible, as only four states have been identified in both molecules.

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Table I. Hartree-Fock Energies for the States of Cu and Cu^+.

State	Basis Set I[a] Energy[e]	ΔE[f]	Basis Set II[b] Energy	ΔE	Basis Set III[c] Energy	ΔE	Exp[d] ΔE
Cu (^2S)	-1638.8025	0.0	-1638.8124	0.0	-1638.8365	0.0	0.0
Cu (^2D)	.7632	1.07	.7714	1.12	.8222	0.39	1.48
Cu^+ (^1S)	.5734	6.23	.5771	6.40	.6004	6.42	7.72
Cu^+ (^3D)	.4853	8.63	.4990	8.53	.5525	7.73	10.54
Cu^+ (^1D)	.4659	9.16	.4817	9.00	.5371	8.15	10.97

[a]Wachter's [8s6p2d] basis set contracted (62111111/511211/32) from reference 8.

[b]Basis I augmented with an additional 3d gaussian with exponent 0.1491 as suggested by Hay in reference 9.

[c]Basis II with the 3d basis function exponents optimized for the ^2D state and contracted (411) as given in reference 9.

[d]The ^2D and ^3D excitation energies are statistical averages of the fine structure levels from reference 10.

[e]Atomic units.

[f]Electron volts.

Table II. Spin-Orbit Hamiltonian Matrix for $^1S + {}^{1,3}L$ or $^2S + {}^2L$

$^{2S+1}A_\Omega$	$^3(\Omega-1)_\Omega$	$^3\Omega_\Omega$	$^3(\Omega+1)_\Omega$	$^1\Omega_\Omega$
$^3(\Omega-1)_\Omega$	$E[^3(\Omega-1)] + (\Omega-1)\frac{\zeta}{2}$	$\sqrt{(L+\Omega)(L-\Omega+1)} \cdot \frac{\zeta}{2/2}$	0	$-\sqrt{(L+\Omega)(L-\Omega+1)} \cdot \frac{\zeta}{2/2}$
$^3\Omega_\Omega$	$\sqrt{(L+\Omega)(L-\Omega+1)} \cdot \frac{\zeta}{2/2}$	$E[^3\Omega]$	$\sqrt{(L-\Omega)(L+\Omega+1)} \cdot \frac{\zeta}{2/2}$	$\Omega\frac{\zeta}{2}$
$^3(\Omega+1)_\Omega$	0	$\sqrt{(L-\Omega)(L+\Omega+1)} \cdot \frac{\zeta}{2/2}$	$E[^3(\Omega+1)]-(\Omega+1)\frac{\zeta}{2}$	$\sqrt{(L-\Omega)(L+\Omega+1)} \cdot \frac{\zeta}{2/2}$
$^1\Omega_\Omega$	$-\sqrt{(L+\Omega)(L-\Omega+1)} \cdot \frac{\zeta}{2/2}$	$\Omega\frac{\zeta}{2}$	$\sqrt{(L-\Omega)(L+\Omega+1)} \cdot \frac{\zeta}{2/2}$	$E[^1\Omega]$

Table III. Hartree-Fock Energies for the $3d^{10}$ and $3d^{9}4s$ States of CuCl.

State	Basis Set I Energy[a]	ΔE[b]		Basis Set II Energy	ΔE		Basis Set III Energy	ΔE	
$X^1\Sigma$	-2098.3376	0.0		-2098.3462	0.0		-2098.3686	0.0	
$^3\Sigma$	.2802	1.56	0.0	.2961	1.36	0.0	.3455	0.63	0.0
$^3\Pi$	.2734	1.75	0.19	.2894	1.55	0.19	.3383	0.82	0.19
$^3\Delta$	.2663	1.94	0.38	.2819	1.75	0.39	.3314	1.01	0.38
$2^1\Sigma$[c]		2.04	0.48				.3306	1.03	0.40
$^1\Pi$	.2583	2.16	0.60	.2762	1.91	0.55	.3265	1.15	0.52
$^1\Delta$	.2539	2.28	0.72	.2707	2.05	0.69	.3207	1.30	0.67

[a]Atomic units.

[b]Electron volts.

[c]Obtained from a frozen core Hartree Fock calculation using the $^3\Sigma$ core orbitals.

Table IV. Recommended Assignments and Excitation Energies for the Low-lying Excited States of CuCl and CuF

	CuCl		CuF	
Present Assignment	Previous Assignment[a]	T_e (eV)	Previous Assignment[b]	T_e (eV)
$^1\Delta_2$		3.3 ± 0.15		2.85 ± 0.15
$^1\Pi_1$	$F\,^1\Pi$	3.1350	violet	2.659
$^1\Sigma_o^+$	$E\,^1\Sigma^+$	2.8609	$B\,^1\Sigma^+$	2.4473
$^3\Delta_1$	$D\,^1\Pi$	2.8479	$C\,^1\Pi$	2.5118
$^3\Delta_2$		2.73 ± 0.02		2.39 ± 0.02
$^3\Delta_3$		2.64 ± 0.02		2.31 ± 0.02
$^3\Pi_o^-$		2.64 ± 0.02		2.27 ± 0.02
$^3\Pi_o^+$	$C\,^1\Sigma^+$	2.5580	$^1\Sigma^+$	2.184
$^3\Pi_1$	$B\,^1\Pi$	2.5397	$A\,^1\Pi$	2.1755
$^3\Pi_2$		2.48 ± 0.02		2.11 ± 0.02
$^3\Sigma_o^+$		2.364 ± 0.003		1.80 ± 0.01
$^3\Sigma_1^+$	$A\,^1\Pi$	2.3559	red	1.79
$^1\Sigma_o^+$	$X\,^1\Sigma^+$	0	$X\,^1\Sigma^+$	0

[a] References 4-6, 14.

[b] References 14 and 15.

Figure 1. Spin-Orbit Coupling in the Excited States of CuCl.